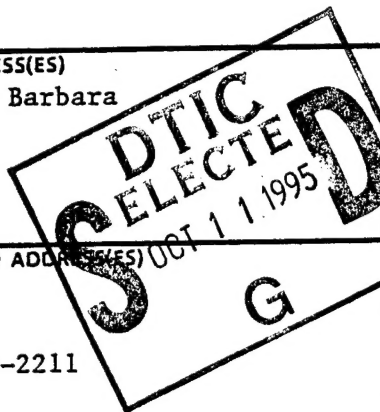


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13. ABSTRACT (Maximum 200 words) This report summarizes studies of model oxidative and hydrolytic reactions for destruction of sulfides and phosphorus (V) compounds. Effects of micelles, solvents, and acid catalysts have been treated quantitatively. Nonmicellizing amphiphiles increase the reactivity of OH ⁻ towards thiol and thione esters.				
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Clifford A. Bunton
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The elucidation of the factors that control micellar effects on reaction rates was a major part of the project. It involved tests of a theoretical treatment based on solution of the Poisson-Boltzmann equation which had been developed earlier with support from ARO. The reactions were dephosphorylations, largely by OH^- and HO_2^- (1, 4, 5, P3), and oxidations of organic sulfides (2,5,P1,P2).

Oxidations of sulfides by HSO_5^- (OXONE) and periodate ion and of thiocarboxylic, thiophosphate and thiophosphinate esters by HSO_5^- have been examined in the absence of micelles. Effects of environment and substrate structure have been established (7, P5, P6). Sulfide oxidations by HSO_5^- and periodate ion have also been examined in zwitterionic betainesulfonate micelles and the data are treated by using a pseudophase model (9). Our conclusion is that micelles and similar association colloids will not provide useful media for oxidation of sulfur compounds by HSO_5^- or periodate ion because although reagents can be solubilized, especially by cationic micelles, rate constants at the micelle-water interface are lower than in water so that overall rate-enhancements are low. Cationic and betainesulfonate micelles behave similarly in these and similar reactions.

As a result of our experimental and theoretical work on micelles and on the mechanisms of dephosphorylation and sulfide oxidation we can predict qualitatively the effects of micelles and other association colloids on these reactions. In particular this treatment is being used to show that rate enhancements of dephosphorylation by mononuclear metallomicelles are due to concentration effects at the micelle-water interface and not to enhancement of nucleophilicity by the micelles (10).

Hydrogen peroxide is a potentially useful decontaminant as a dephosphorylating agent in the form of HO_2^- at high pH (4,6,P4) and as an oxidant for organic sulfides in acidic solution. The acid can be H_2SO_4 or an acidic ion-exchange resin (P6). The advantage of the latter is that the catalyst is reusable. We continue to explore this system.

Work which is in progress, and has not been described in either preliminary or final form, includes a study of solvent effects on nucleophilic dephosphorylations by OH^- or oximate ions. This work complements the micellar work in that the treatment of thickened agents requires the use of surfactant-derived association colloids or organic solvents. Contrary to predictions of quantitative kinetic models and the Hughes-Ingold Rules these nucleophilic dephosphorylations are inhibited by addition of organic solvents (MeCN or t-BuOH) to water. We believe that this inhibition is due to initial state stabilization of the hydrophobic substrate and we are trying to fit the data quantitatively on this hypothesis. Rate constants go through minima with decrease of the water content of the solvent due to eventual desolvation of the anionic nucleophile.

Nonmicellizing amphiphiles (cationic phase transfer catalysts) speed reactions of OH^- with thiol and thione phosphorus (\bar{V}) esters and the dependence of rate on amphiphile concentration is qualitatively similar to those observed with cationic micelles (1,4,5,11).

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